



# PATENT SPECIFICATION

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[Divided out of No. 581,410].

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## COMPLETE SPECIFICATION

### Curing of Polymeric Materials.

We, DAVID AUGUSTINE HARPER and WALTER FAIRBAIRN SMITH, both of Hexagon House, Blackley, Manchester, British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the curing of polymeric materials more especially to the curing of organic diisocyanate modified poly-esteramides in admixture with other polymeric materials.

In Application numbered 13204/41 (Serial No. 580,524) it has been proposed to cure organic diisocyanate modified polyester-amides by heating these in the presence of formaldehyde or of a formaldehyde-liberating substance, and preferably, also in the presence of materials which function as curing catalysts, for example, formic, glycollic, oxalic, succinic, maleic, adipic, tartaric, salicylic, anthranilic, phthalic, citric, boric and phosphoric acids, phthalic and maleic anhydrides, phthalimide and potassium or sodium dihydrogen phosphate.

In Application numbered 7392/42 (Serial No. 580,526) it has been proposed to cure organic diisocyanate modified polyester-amides by heating these in the presence of formaldehyde or of a formaldehyde-liberating substance and also in the presence of curing catalysts which are substantially neutral but which develop acidity only under curing conditions, for example, butadiene sulphone, 2:3-dimethylbutadiene sulphone, butadiene-tetrabromide, styrenedibromide, acetylene tetrabromide, tribromohydroquinone, 1-bromo-2-naphthol, 1:6-dibromo-2-naphthol, 1:4:6-tribromo-2-naphthol, 2:4-dibromo-1-naphthol, methyl- $\alpha$ : $\beta$ -dibromopropionate,  $\beta$ -chloroethyl- $\alpha$ : $\beta$ -dibromoisobutyrate, ethyl  $\alpha$ -bromo-propionate, phenyl trichloroacetate,  $\alpha$ : $\alpha$ : $\beta$ -trichloropropionitrile, trichloroacetamide, trichloroacetyldiethylamide, N-trichloroacetylanilide, N:N'-di(trichloroacetyl)

methylenediamine, N:N'-di-(trichloroacetyl)ethylenediamine, interpolymers of asymmetrical dichloroethylene and vinyl chloride, and chloranil tetrachloro-p-benzoquinone).

In Application numbered 10290/43 (Serial No. 581,146) it has been proposed to use dichromates for curing organic diisocyanate modified polyester-amides.

We have now found that the organic diisocyanate modified polyester-amides may be cured, with advantage, together with small or large proportions of other polymeric materials which are themselves reactive to formaldehyde and/or dichromates.

According to the present invention in the curing of organic diisocyanate modified polyester-amides in the manner hereinafter set forth we provide the improvement which comprises curing said modified polyester-amides in uniform admixture with a proportion of a derivative of cellulose.

The invention also comprises heat-curable compositions comprising as the essential ingredients an organic diisocyanate modified polyester-amide, a proportion of a derivative of cellulose, and one or more materials of the kind hereinafter set forth such as are customarily used for curing organic diisocyanate modified polyester-amides.

Water-soluble or water-insoluble derivatives of cellulose include cellulose esters, for example, cellulose nitrate and cellulose acetate, and cellulose ethers such as benzyl cellulose. These materials are modified by the action of formaldehyde thereon, and they are compatible with the organic diisocyanate modified polyester-amides, in the sense that they are capable of forming homogeneous blends there-with.

The derivative of cellulose may be brought into uniform admixture with the organic diisocyanate modified polyester-amide in several ways. For instance, a derivative of cellulose dissolved in water is slowly added to an organic diisocyanate modified polyester-amide running on a warm rubber mill. Or, a derivative of cellulose in powder form, is milled into an

organic diisocyanate modified polyester-  
amide on a rubber mill, a sufficiency of  
water usually being added to render the  
mix soft. When water is used before or  
during the incorporation, the mix is  
usually milled until it is substantially  
dry, the rolls, if hot, being preferably  
allowed to cool during the drying so as to  
minimise the risk of the mix sticking  
thereto. Alternatively, the components  
are mixed or milled together (in the  
absence of water) as such or in the  
presence of organic liquids which are sol-  
vents for one or more of the materials; the  
organic liquids are removed as and when  
convenient.

The proportions of the components are  
not critical, but usually from about 25 to  
175 parts of the derivative of cellulose per  
100 parts of organic diisocyanate modified  
polyester-amide are used.

The mixtures are cured by means of  
any of the materials customarily used for  
curing organic diisocyanate modified  
polyester-amides, that is to say, by heat-  
ing with a known curing agent, namely,  
formaldehyde or a formaldehyde-liberat-  
ing substance or a dichromate, preferably  
in the presence of a known curing cata-  
lyst, namely, an acid or a material which  
is substantially neutral but which  
develops acidity under curing conditions.  
These ingredients required for curing are  
incorporated with the mix whenever con-  
venient, but, if water has been used to  
assist in the formulation of the mix, pre-  
ferably after the mix is dried.

As well as those already mentioned, one  
or more additional compounding ingre-  
dients may also be used. These include  
fillers, for example, carbon black, iron  
oxide, clay, asbestos, blanc fixe, whiting,  
lithopone and mica; resins, for example,  
urea-formaldehyde and phenol-formalde-  
hyde resins; other plastic materials, for  
example, natural or synthetic rubbers,  
vulcanised vegetable oils, dark substitute,  
white substitute, a Cumar resin, wood  
rosin and pitch; de-tackifying agents,  
that is to say, materials which reduce the  
tendency of the mix to stick to the rolls,  
for example, stearic acid, paraffin wax,  
oleic acid, lauric acid and dibutyl  
ammonium oleate; plasticisers, for  
example, tricresyl phosphate, dibutyl  
phthalate, butylphthalyl butyl glycol-  
late, and N-alkyl-toluenesulphonamides;  
stabilisers or anti-oxidants, for example,  
hydroquinone, N,N'-hexamethylene-bis-  
ortho-hydroxy-benzamide, N-phenyl- $\alpha$ -  
naphthylamine, N-phenyl- $\beta$ -naphthyl-  
amine and  $\alpha$ : $\alpha$ -bis(2-hydroxy-3:5-  
dimethylphenyl)butane, as well as others  
commonly used in rubber technology.  
Small quantities of pigments, for example

from 1-3% by weight, such as are  
customarily used in rubber technology or  
in the coating composition art may also be  
used to impart colour. The use of alkaline  
reacting compounding ingredients should  
be avoided since these may cause degrada-  
tion of the polymeric materials.

When the ingredients are mixed, the  
mix is removed from the mill or mixer, if  
desired, formed into shapes or spread or  
calendered on to a substrate, for example  
on to the surface of a fabric, or on to the  
surface of a coated fabric and then curing  
is effected by heating, for example, in a  
mould which is preferably in a hydraulic  
press, or in hot air. Periods of heating  
varying from a few minutes to several  
hours at 100-150° C. are usual. If  
desired, to facilitate shaping or spreading,  
organic solvents or swelling agents or  
additional solvents or swelling agents  
may be incorporated with the materials;  
these are removed as and when convenient.

Suitable organic solvents include  
acetone, mixtures of benzene and acetone,  
mixtures of benzene and ethanol, mixtures  
of benzene and chloroform, mixtures of  
benzene and methylethyl ketone, mixtures  
of methyl ethyl ketone and trichloro-  
ethylene, and mixtures of acetone and the  
monoethyl ether of ethylene glycol.

Polyester- and polyamide-forming  
reactants suitable for making the diiso-  
cyanate modified polyester-amides to be  
used for the purposes of the present inven-  
tion include glycols, for example,  
ethylene glycol, diethylene glycol, tri-  
methylene glycol, pentamethylene glycol,  
hexamethylene glycol, dodecamethylene  
glycol, 1:12-octadecanediol and penta-  
glycol; aliphatic or aromatic amino-  
alcohols having at least one hydrogen  
atom attached to the amino nitrogen atom  
and preferably containing an aliphatic  
chain of at least two carbon atoms separat-  
ing the amino and hydroxyl groups, for  
example  $\beta$ -ethanolamine and 3-amino-  
propanol; dibasic carboxylic acids or ester-  
forming derivatives thereof, preferably  
aliphatic dicarboxylic acids, for example,  
malonic, succinic, glutaric, adipic,  $\beta$ -  
methyladipic, pimelic, suberic, azelaic,  
sebacic, undecanedioic, brassylic, iso-  
phthalic, hexahydroterephthalic, *p*-  
phenylenediacetic, and acetone-dicarb-  
oxylic acids; primary and secondary  
diamines, for example, ethylene diamine,  
hexamethylenediamine, 3-methylhexa-  
methylene diamine, decamethylenedi-  
amine, *m*-phenylenediamine, N,N'-di-  
methylhexamethylenediamine, N,N'-di-  
ethylhexamethylenediamine, and N,N'-  
dimethyldecamethylenediamine; mono-  
hydroxymonocarboxylic acids or their  
ester-forming derivatives, for example, 130

glycollic, 6-hydroxycaproic, 10-hydroxydecanoic and 12-hydroxystearic acids; polymerizable monoaminomonocarboxylic acids, or their ester-forming derivatives, for example, 6-aminocaproic acid or its lactam, caprolactam, and 9-aminononanoic, 11-aminoundecanoic and 12-aminostearic acids.

The polyester-amides are made in known manner by heating the selected reactants at polymerizing temperatures, usually in the absence of air or oxygen, under conditions whereby water is removed from the reaction mixture. When a diamine is to be used, it is conveniently used in the form of the corresponding diammonium salt from some of the dibasic carboxylic acid to be used.

The polyester-amides are modified with organic diisocyanates in known manner for example, by mixing them, for example by stirring, milling or kneading, with the organic diisocyanate and then heating the mixture, for example, to a temperature of 100—200° C. for a period of 10—720 minutes. Up to about 10 per cent., usually 3—7%, by weight of the diisocyanate is used.

Examples of organic diisocyanates includes ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, decamethylene diisocyanate, *p*-phenylene diisocyanate, *m*-phenylene diisocyanate, *p*:*p*<sup>1</sup>-diphenyl diisocyanate, diphenylmethane-4:4<sup>1</sup>-diisocyanate, naphthalene diisocyanates and adipyl diisocyanate.

The new heat-curable compositions of the invention may be used in the fabrication of a variety of articles, in which they may or may not be supported on a substrate and/or interspersed with fillers. For instance, they may be used in the construction of organic liquid resistant articles of all kinds, for example, gaskets, packings, hose, diaphragms for pumps and the like, as well as in the fabrication of flexible containers. They may also be used in the coating of rollers, blankets and stereos for use in the printing industry, or to provide protective sheathings for insulated electric cables and other electrical conductors. They also find application in the coating of the balls for games, tyres and flexible materials generally, including fabrics, protective clothing, leather cloth and floor coverings, and generally in the construction of articles requiring the use of a material having physical properties resembling those of rubber, but also having a good resistance to the action of organic fluids and a low permeability to gases and vapours.

They are well adapted for application in the form of lacquers or finishing com-

positions for all kinds of surfaces. They may be formed into films or sheets, for example, as substitutes for leather or as wrapping films, and they may be used as adhesives for a wide variety of materials, for example, wood, metals, fabrics, paper, leather and regenerated cellulose.

The invention is illustrated but not limited by the following Examples, in which the parts and percentages are expressed by weight, unless otherwise stated:—

#### EXAMPLE 1.

Into 100 parts of an organic diisocyanate modified polyester-amide there are milled 10 parts of titanium dioxide, 5.0 parts of hexamethylolmelamine hexamethyl ether and 0.75 parts of 2:4-dichloro-1-naphthol. The mix is then let down in 100 parts of a mixture of equal volumes of benzene and acetone, and 125 parts of a 20% solution of cellulose acetate (acetone-soluble) are stirred in. The mix is thinned with acetone to a solids content of 10—15% and is ready for use.

The composition is flowed on to a glass plate, the solvent is allowed to evaporate, and the so obtained film is cured by heating in air at 125° C. for 2 hours.

The cured film is tough and has a rubbery handle; its surface is very resistant to scratching.

When the recipe of the Example is repeated using twice the quantity of the solution of cellulose acetate, a film is obtained which is tougher, less rubbery, harder, and extremely resistant to scratching.

Similarly, when the recipe of the Example is repeated using three times the quantity of the solution of cellulose acetate, there is an increase of toughness and hardness, and a decrease of rubbery properties; the film has outstanding resistance to scratching.

#### EXAMPLE 2.

Into 100 parts of an organic diisocyanate modified polyester-amide there are milled 10 parts of titanium dioxide, 5.0 parts of hexamethylolmelamine hexamethyl ether and 0.75 parts of 2:4-dichloro-1-naphthol. The mix is let down in 100 parts of a mixture of equal volumes of benzene and acetone, and 250 parts of a 20% solution of nitrocellulose obtainable commercially under the name "Collodion Cotton HX 30/50" are stirred in. The mix is thinned with acetone to a solids content of 10—15% and is ready for use.

The composition is flowed on to a glass plate, the solvent is removed by evaporation, and the so obtained film is cured by heating in air at 125° C. for 2 hours.

The cured film is tough, rubbery and

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95

100

105

110

115

120

125

130

has a very good scratch resistance.

When the recipe of the Example is repeated using half as much again of the nitrocellulose solution, a tougher, less rubbery film with better scratch resistance is obtained.

EXAMPLE 3.

A lacquer is prepared by mixing together 100 parts of an organic diisocyanate modified polyester-amide, 60 parts of the cellulose acetate used in Example 1, 10 parts of carbon black, 5 parts of hexamethylmelamine hexamethyl ether, 0.75 parts of 2:4-dichloro-1-naphthol, 200 parts of ethylene glycol monoethyl ether and 350 parts of acetone.

The so obtained lacquer is used to provide a top-coating for the hydrolysed leather-organic diisocyanate modified polyester-amide coated fabric obtained in the manner set forth in Application numbered 21389/43. (Serial No. 588,862), and more specifically as follows:—

130 parts of disintegrated scrap vegetable-tanned leather are mixed with sufficient cold water to form an easily stirred slurry, the slurry is heated up to boiling and boiled for about 5 minutes. The leather settles in the form of a crumbly mass from which the liquid is poured off. The wet mass is added in small amounts to 100 parts of an organic diisocyanate modified polyester-amide running on to a rubber mill with the rolls heated to about 70° C.; the mix is milled until homogeneous, and then dried on the rolls. The following ingredients are then added in the order listed, 0.5 parts stearic acid, 30 parts of titanium dioxide, 5 parts of hexamethylmelamine hexamethyl ether and 0.75 parts 2:4-dichloro-1-naphthol, milling is continued until the mix is again homogeneous, and it is then sheeted off the mill.

The sheet is added to its own weight of a benzene-ethanol mixture (75:25 by volume) in a Werner Pfeleiderer mixer, and mixed until a smooth dough is

obtained. The dough is spread on to a cotton twill fabric, the organic liquids are allowed to evaporate.

The coated spreading is then cured by heating in air at 125—130° C. for 2 hours.

The cured material has a high gloss, an excellent abrasion, scrub and flex resistance, and an outstanding resistance to scratching or marking.

The organic diisocyanate modified polyester-amide used in the above Examples is that described in Example 7 of Application numbered 13204/41 (Serial No. 580,524).

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the process of curing organic diisocyanate modified polyester-amides in the known manner hereinbefore set forth, the improvement which comprises curing said modified polyester-amides in uniform mixture with a proportion of a derivative of cellulose.

2. The improvement which comprises curing organic diisocyanate modified polyester-amides in uniform admixture with a proportion of a derivative of cellulose in the manner hereinbefore particularly described and ascertained especially with reference to the foregoing Examples.

3. Organic diisocyanate modified polyester-amides whenever cured in uniform admixture with a proportion of a derivative of cellulose according to either of the preceding claims.

4. Heat-curable compositions comprising as the essential ingredients an organic diisocyanate modified polyester-amide, a proportion of a derivative of cellulose, and one or more materials of the kind hereinbefore set forth such as are customarily used for curing organic diisocyanate modified polyester-amides.

Dated the 28th day of September, 1945.

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Solicitor for the Applicants.